

Thermodynamic models for water sorption by garlic

Sadhna Arora · Sajeev Rattan Sharma · Satish Kumar

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Abstract Moisture sorption characteristics of garlic grown in Punjab region of India were evaluated at 20–60⁰ C and water activity of 0.2–0.9. The samples were equilibrated using aqueous glycerol solution. Equilibrium moisture content of garlic decreased with an increase in temperature at constant water activity. The data was adjusted to nine sorption models to ascertain the best fit. Comparisons were based on mean relative error, standard error and coefficient of determination. Of the models tested, Oswin model showed best fit. The isosteric heat of sorption decreased with moisture content. Isokinetic temperature and free energy were determined using plots of enthalpy and entropy.

Keywords Garlic · Equilibrium moisture content · Oswin model · Moisture sorption · Water activity · Isosteric heat

Introduction

Garlic (*Allium sativum* L.) is a bulbous perennial and is valued for its flavour and widely applied in food and pharmaceutical preparations. Garlic has been used throughout history for the treatment of a wide variety of ailments, including hypertension, headache, bites, worms and tumours. Garlic is a rich source of carbohydrates, protein and phosphorus (Dhingra and Paul 2006).

The knowledge of sorption properties of a material is essential in studies on drying of foods especially in the

presence of solid additives. These additives can play either a protective role against thermal shock during drying, modify product properties or simply decrease moisture content in the final products. Contact drying and contact-sorption drying are examples of special drying techniques where moisture equilibrium has direct effect on drying technique and technology. The ability of biological materials to resist deterioration in the quality not only depends upon material properties but also environmental condition during storage and processing. Information on sorption isotherm is important in design of drying processes and microbiological safety (Rizvi 1986). Due to complexity of food composition, theoretical prediction of moisture isotherm is not possible and hence not only experimental measurements but also moisture sorption isotherm equations are necessary for prediction of quality of stored foods. When water vapour is sorbed on a surface, a quantity of heat known as, the heat of sorption is released. When sorbed water vapour is desorbed a quantity of heat known as heat of desorption is taken up. Heat of sorption and desorption is measure of the heat or energy that must be added to adsorbed gas to break the intermolecular force. The isosteric heat of sorption is quite a valuable tool in understanding the mechanism of sorption. It can be defined as the amount of energy required to remove water from the substrate in excess of the amount of the energy required for normal water vaporization. Hence it is the assessment of the binding energy between water molecules and the solid matter of a food product. The isosteric sorption heat represents the difference between the net isosteric heat and pure water vaporization energy. A lot of theoretical and empirical equations have been developed for describing relationship between moisture content and water activity of different products for example, whole pistachio nuts (Maskan and Karatas 1997), banana (Kechaou and Maales

S. Arora (✉) · S. R. Sharma · S. Kumar
Department of Processing and Food Engineering,
Punjab Agricultural University,
Ludhiana 141 004, India
e-mail: arora_sadhna@rediffmail.com

1999), garlic (Vazquez et al. 1999), okra (Fahrettin and Maskan 1999), vegetable wastes (Lopez et al. 2000), flax straw (Nilsson et al. 2005), flax/linseed (Kymalainen and Pastila 2000), watermelon seeds (Wani et al. 2006), stone fruit (Phomkong et al. 2006) and rough rice (Yu and Wang 2006). Limited information is available on water sorption characteristics and isosteric heat of adsorption of garlic. The present work aimed to obtain sorption isotherms at selected temperatures to determine the goodness of fit of selected sorption isotherm models for garlic. The net isosteric heat of sorption of different moisture levels was also evaluated.

Materials and methods

Garlic (*Allium sativum* L.) cv PG-117 was obtained from the experimental fields of the university. Garlic was cleaned, split and peeled. The initial moisture content of garlic was around 235% (db). Sample (2 kg) was kept as fresh for determination of desorption isotherms. The rest of the garlic was dried at 40 °C and air velocity of 2 m/s in a Kilburn make laboratory tray drier to a constant weight. Selection of 40 °C was based on the assumption that at 40 °C it affects on water sorption characteristics of garlic to the minimum. The moisture content of garlic after drying was about 10% dry basis. Some samples of dried whole garlic were kept and rest was ground to a fine powder. Dried whole garlic and powder were used to study the adsorption isotherm. Thus the three prepared samples were then used in determination of equilibrium moisture content (EMC) at 20, 30, 40, 50 and 60 °C temperatures and 0.2–0.9 water activity (a_w) using static method. For maintaining the desirable RH, aqueous glycerol solutions of different concentrations were used (Lapinski et al. 1976). The dessicators containing the glycerol solution and 5 g of sample were placed in hot air oven and

incubator depending upon the selected temperature. The temperature and RH during experimentation were measured with digital hygrometer. Partial vacuum was created inside each dessicator to accelerate the adsorption or desorption process. The samples were weighed using an electronic single weighing balance with an accuracy of 0.001 g at an interval of 72 h. The equilibrium was judged to have been attained when the change in subsequent reading was less than 5 mg. In general, 15–20 days were required to reach equilibrium with surrounding environment. Moisture content was determined using standard method (AOAC 2000). Each experiment was replicated thrice and average values were used in the analysis.

The models selected to fit the EMC data of garlic are presented in Table 1. These models were selected on the basis of their effectiveness to describe the sorption isotherms of foods like cereals, fruits and vegetables (Iglesias and Chirife 1982; Lopes Filho et al. 2002).

Thermodynamic properties of sorption The isosteric heat of sorption (Q_{st}) is a thermodynamic parameter obtained from equilibrium sorption data and represents the discrepancy between latent heat of sorption and the latent heat of condensation of pure water.

The study of sorption isotherms at least at two different temperatures provides thermodynamic data on isosteric heat of sorption through use of the integrated form of Clausius—Clapeyron equation

$$\ln\left(\frac{aw_1}{aw_2}\right) = -(q_{st}/R) \left[\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right) \right] \tag{1}$$

where $q_{st} = Q_{st} - \Delta H_{vap}(H_2O)$

In these two equations aw_1 and aw_2 are the water activities at given moisture content at temperature T_1 and

Table 1 Data on goodness-of-fit of selected sorption isotherm models for garlic at selected temperatures and water activity

Isotherm	Equation	Reference
Oswin	$m = c \times \left(\frac{a_w}{1-a_w}\right)^n$	Oswin (1946)
Smith	$m = a - b \times \ln(1 - a_w)$	Smith (1947)
Chen-Clayton	$m = \left(\frac{-1}{(c \times t^d)}\right) \times \left(\ln\left(\frac{\ln(a_w)}{-a \times t^b}\right)\right)$	Chen and Clayton (1971)
Chung-Pfost	$m = e - f \times \ln(-(t + c) \times \ln(a_w))$	Chung and Pfost (1976)
Henderson	$m = \left(\frac{\left(\frac{\ln(1-a_w)}{-k \times (t+c)}\right)^A}{100}\right) (1/n)$	Henderson (1952)
GAB	$m = \frac{m_1 \times g \times f \times a_w}{[(1-f \times a_w)(1-f \times a_w + f \times g \times a_w)]}$	Maskan and Karatas (1997)
BET	$m = \frac{a \times b \times a_w}{(1-a_w) \times (1+(b-1) \times a_w)}$	Kechaou and Maales (1999)
Halsey	$m = \left[\frac{-(\exp(a-c \times t))}{\ln(a_w)}\right]^A \left(\frac{1}{b}\right)$	Halsey (1946)
Iglesias and Chirife	$m = \frac{[\exp(b \times a_w + p)]^{A+2} + m_o}{2 \times \exp(b \times a_w + p)}$	Iglesias and Chirife (1982)

T_2 , respectively. Q_{st} is the isosteric heat of sorption, q_{st} is the net isosteric heat of sorption or enthalpy of sorption, ΔH_{vap} (H_2O) is the enthalpy of vaporization of water and R is the universal constant. The important term here is the isosteric heat of sorption, which is a measure of interaction between water vapour and the adsorbent food material. It is an important parameter whose values show that at the end of the drying it can not be neglected in energy balance since it has the same order of magnitude as the vaporization latent heat.

The use of Clausius-Clapeyron equation implies that the moisture content of the system under consideration remains constant and that the enthalpy of vaporization of pure water

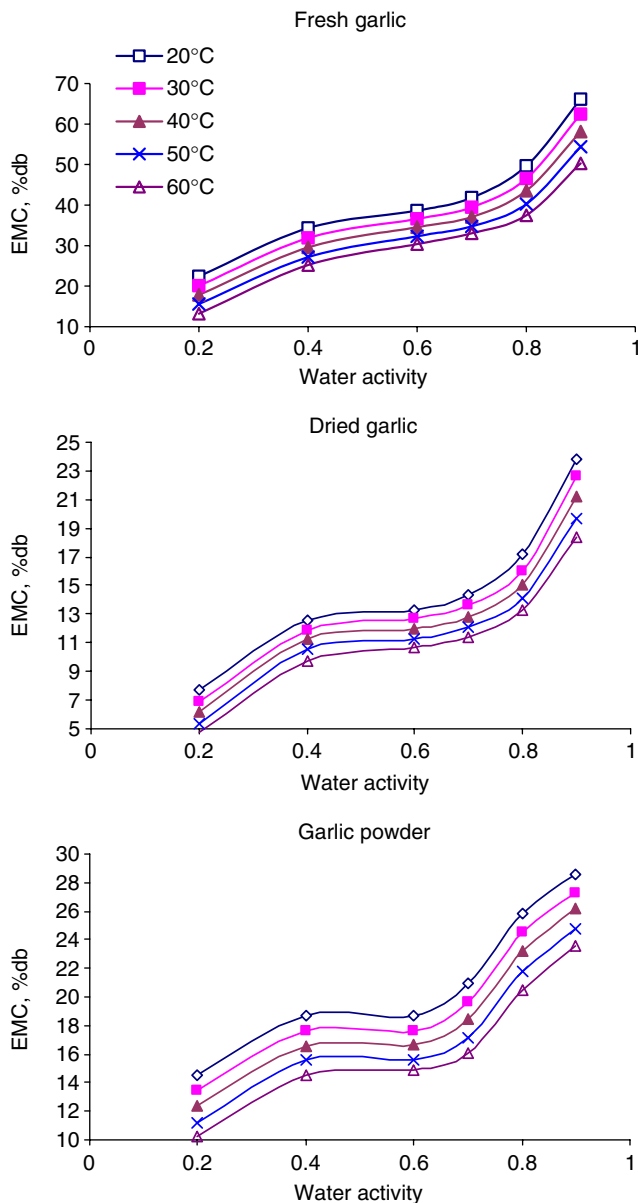


Fig. 1 Sorption isotherms of garlic at different temperatures. EMC: Equilibrium moisture content

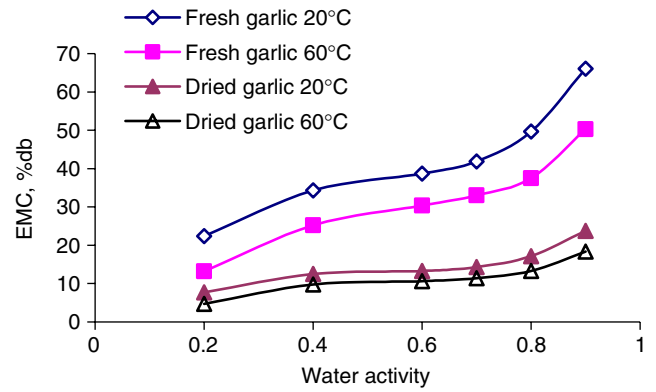


Fig. 2 Hysteresis effect shown by garlic

(as well as the excess heat of sorption) does not change with temperature.

The change in molar differential entropy of desorption can be calculated from Gibbs-Helmholtz equation

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{2}$$

The free energy is calculated from Gibb's equation

$$\Delta G = RT \ln a_w \tag{3}$$

Substituting the value of ΔG in Eq. 2 and rearranging the equation takes the form

$$\ln a_w = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{4}$$

Table 2 Coefficients of Oswin model for sorption isotherms of data for garlic

Treatment	Temp, °C	c	n	R ²
Fresh garlic	20	34.68	0.2806	0.9743
	30	32.12	0.2937	0.9723
	40	29.62	0.3059	0.9683
	50	27.01	0.3230	0.9610
	60	24.58	0.3446	0.9437
Dried garlic	20	12.14	0.2822	0.9488
	30	11.30	0.2957	0.9427
	40	10.48	0.3086	0.9312
	50	9.66	0.3212	0.9212
	60	8.89	0.3352	0.9148
Garlic powder	20	18.82	0.1864	0.9385
	30	17.66	0.1937	0.9405
	40	16.56	0.2032	0.9434
	50	15.38	0.2119	0.9398
	60	14.34	0.2224	0.9478

Table 3 Constants for the temperature dependent forms of the Oswin coefficients of garlic

Product	c_o	ΔH_1 , kJ/mol	n_o	ΔH_2 kJ/mol	T_B , K	ΔG_B , kJ/mol
Fresh garlic	2.00	-6.97	1.49	4.09	370.98	0.0607
Dried garlic	0.92	-6.31	1.17	3.46	387.87	0.0749
Garlic powder	1.97	-5.52	0.81	3.59	364.92	0.0606

So, the isosteric heat of sorption or enthalpy of sorption can be calculated from Eq. 4 by plotting $\ln a_w$ versus $1/T$ for certain values of moisture content and then determining the slope, which is equal to $-\Delta H/R$, the linear coefficient being equal to $\Delta S/R$.

Results and discussion

Figure 1 shows that EMC of garlic increased with a_w . This may be due to the fact that vapour pressure of water present in foods increases with that of surroundings. All isotherm curves followed the same sigmoid shape thus reflecting the prevalent Type II isotherm characteristics. The EMC values decreased with increased temperature at all levels of water activity. The reason may be that temperature increased the vapour pressure of moisture within the garlic and hastened the transfer of moisture from sample to the air. It is observed that the sorption characteristics are dependent on the direction of attaining the equilibrium moisture content. The kinetic energy associated with water molecules present in foods increases with increasing temperature at a given water activity. On comparison of dried whole garlic and dried garlic powder, it was found that garlic powder was more hygroscopic as compared to whole garlic as the EMC value of garlic powder was more at all temperatures and for all RH. For fresh garlic, desorption isotherms were studied. The higher value of EMC of fresh garlic as compared to dried garlic at all temperatures may be due to higher initial moisture content. This phenomenon is similar to the fact that desorption equilibrium is higher than the adsorption equilibrium and this may also reflect the hysteresis effect. Figure 2 shows the hysteresis effect between fresh and dried garlic at 20 and 60^o C. This effect is exhibited over the entire range of water activities. The hysteresis loop decreased as the temperature increased.

The sorption models presented in Table 1 were tested for their effectiveness to describe the adsorption and desorption isotherms. The regression coefficient models were computed using the least square technique. R^2 , S.E. and E values were calculated for all models and found that E was least for Oswin equation which also showed best fit for R^2 and S.E. The coefficients of Oswin model for sorption isotherms for all the products have been

presented in Table 2. The values of c decreased with temperature while n increased which is in agreement with the results of Pawar et al. (1992) and Maskan and Karatas (1997).

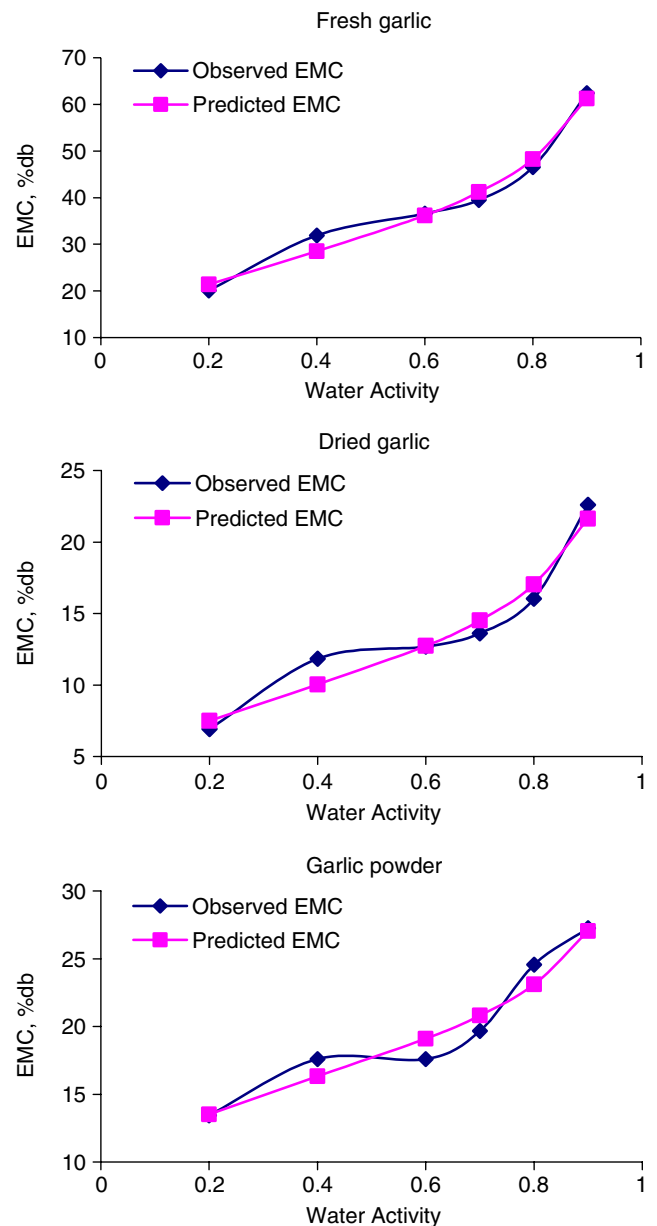


Fig. 3 Observed and predicted values of EMC for garlic at 30 °C. EMC: Equilibrium moisture content

The coefficients c and n of Oswin model were considered for their temperature dependency according to the following correlations.

$$c = c_o \exp \left[\frac{\Delta H_1}{RT} \right] \tag{5}$$

$$n = n_o \exp \left[\frac{\Delta H_2}{RT} \right] \tag{6}$$

where c_o and n_o are constants adjusted for the temperature effect, T is the absolute temperature (K), R is the universal constant (kJ/molK) and ΔH_1 and ΔH_2 are the functions of the sorption heat of water. The values of c and n were fitted to these equations and c_o , ΔH_1 , n_o and ΔH_2 were found out for fresh, dried and powdered garlic with $R^2 > 0.95$ and

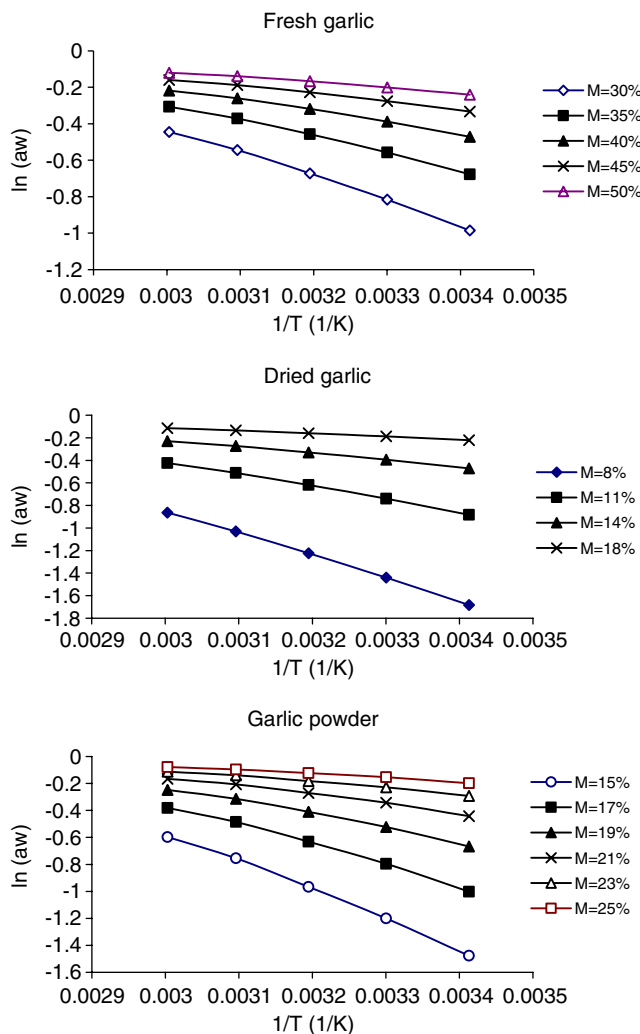


Fig. 4 The Clausius-Clapeyron plot for garlic at selected moisture contents

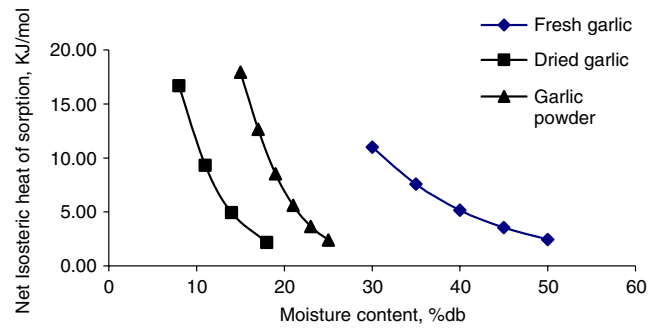


Fig. 5 Net Isosteric heat of sorption for garlic

presented in Table 3. The positive values of ΔH_2 are due to exothermic interaction of water vapour with the primary sorption sites of garlic and negative values of ΔH_1 are due to endothermic interaction.

The observed and predicted adsorption and desorption moisture isotherms by Oswin’s equation at 30 °C are shown in Fig. 3. The agreement between the observed and predicted results was excellent for the RH range of 20–90%. The same trend was observed at all the other temperatures.

Figure 4 represents the sorption isotherms $\ln(a_w)$ vs $1/T$ which should be straight lines at various moisture content values. For each water content, a sorption isostere has been plotted and the isosteric sorption heat was calculated from its slope. For each product, the representation of isosteric heat vs. moisture has then been plotted in Fig. 5. All the results have been co-related satisfactorily by the following relations;

Fresh garlic; $q_{st} = 103.93e^{-0.075m}$, $R^2 = 0.9999$
 Dried garlic; $q_{st} = 86.967e^{-0.2049m}$, $R^2 = 0.9998$
 Garlic powder; $q_{st} = 390.95e^{-0.2029m}$, $R^2 = 0.9988$

The perusal of Fig. 5 shows that the heat of sorption decreased as the moisture content increased. The decrease in the isosteric heat with amount of water sorbed is as a result of sorption occurring on the most active available sites initially. This yields the greatest interaction energy, but

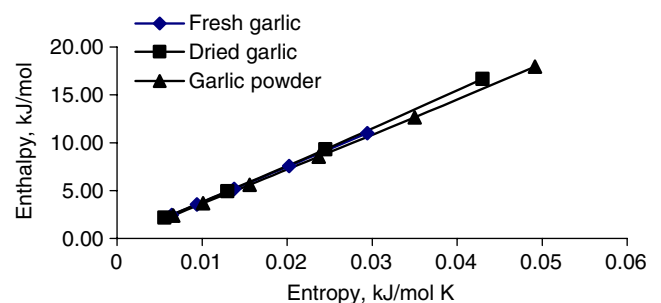


Fig. 6 Enthalpy—Entropy relationship for water sorption in garlic

as sorption progresses, the availability of sorption active sites decreases and lower heat of sorption results. The value for net isosteric heat for fresh garlic was found to be higher than that of dried garlic. This finding substantiates the presence of hysteresis phenomenon during the sorption process.

A plot of ΔH vs ΔS for garlic (Fig. 6) from calculated values of Eq. 4 and Fig. 4 was prepared for each of the product. These values were correlated with Eq. 7:

$$\Delta H = T_B(\Delta S) + \Delta G_B \quad (7)$$

where, T_B is the isokinetic temperature and ΔG_B is the measure of the free energy at T_B . The law of compensation is applicable in the range of moistures studied having the value of $R^2 > 0.99$ (Fig. 6). The isokinetic temperature has an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate. Since, there is high degree of linear correlation between enthalpy and entropy, the compensation theory was assumed to be valid for sorption. T_B and ΔG_B were calculated for all the products and are given in Table 3. The straight lines observed in Fig. 6 at all moisture contents for isokinetic temperature correspond to a zone of sorption controlled by enthalpy.

It can be concluded that the Oswin model was found to give best fit to the experimental data for garlic. The isosteric heat of adsorption and desorption decreased with increase in moisture content. The linear plot of compensation between enthalpy and entropy correlated well for enthalpy controlled mechanisms in sorption.

Conclusion

The sorption isotherms of garlic were studied at temperature range of 20–60 °C and RH range of 20–90%. The EMC values decreased with increase in temperature at constant RH. The moisture isotherms were characteristics of the type II isotherm. The values of desorption EMC was higher than that of adsorption EMC. The hysteresis effect was exhibited over the entire range of RH and it decreased with increase in temperature. The Oswin model was found to give best fit to the experimental data for garlic. The isosteric heat of adsorption and desorption decreased with increase in moisture content. The linear plot of compensation between enthalpy and entropy correlated well for enthalpy controlled mechanisms in sorption.

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